

Evaluation of Cationic and Anionic Polyelectrolytes as a Coagulants Aid for Water Quality Improvement

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ABSTRACT

The water pollution control is one of the major thrust areas of scientific research. The suspended particles which do not undergo biological degradation need special attention. During the last few decades several techniques have been used to remove the suspension; whereas the use of Polyelectrolytes along with inorganic coagulants is one of the most promising techniques. Here, the use of polymers along with inorganic coagulants is reviewed with emphasis on the type of polyelectrolytes i.e. cationic and anionic, molecular mass and charge density, mechanism of coagulation and flocculation and the kinetics aspect of polymers.

Keywords: Polyelectrolytes, Water treatment, Coagulation and Flocculation.

INTRODUCTION

The impurities present in water are in the form of dissolved organic matter¹ or suspended material such as clays, sand, silt, etc^{2,3}. Dissolved organic compounds (DOC) are those compounds which will pass through a membrane having pores of 0.45µm size. DOC poses a problem for the water treatment industry for a number of reasons. Apart from the aesthetic problems of colour, taste and odour, its presence poses a health hazard^{4,5}. It can also block the pores of activated carbon filters, hindering adsorption of trace organic

contaminants such as taste and odour. Suspended matters are an important component of all natural water. Particles can range from 10µm or more down to submicron colloidal size. Such materials need to be removed from water because it supplies a surface on which microbes can be adsorbed and protected from disinfection chemicals by a coating of slime.

These impurities cannot be removed alone by inorganic coagulants. Because most essential drawbacks involve by using inorganic coagulants are low efficiency, high level of water mineralization and large amount of sludge. So, a novel technology

has been developed for the removal of turbidity from water with the addition of polyelectrolytes^{6,7}. The polyelectrolytes in combination with inorganic coagulants have been utilized for coagulation and flocculation methods for water purification for at least four decades⁸. The above combined complexes will be effective and promising for the purification of water and waste water. The polyelectrolytes used in water treatment are water soluble and mainly synthetic in nature⁹, although few natural polyelectrolytes may be of interest. The advantages over the usage of polyelectrolytes are lower coagulation dose requirement, a small volume of sludge, a smaller increase in the ionic load of treated water and cost saving up to 25% to 30%¹⁰⁻¹³.

The aim of this paper is to review the practicalities of polymers used for water treatment with particular attention to the polymer characteristics, types of polyelectrolytes used in water treatment, mechanism of action and kinetic aspects. Detail account of kinetic aspects has been given in the appendix at the end.

Type of Polyelectrolytes Vs Polymer Chain and Charge Density

The most important characteristics of polymeric flocculants are molecular mass and charge density. Molecular mass values range from a few thousands up to tens of millions. Conventionally polymers are regarded as having low, medium and high molecular mass. The range of molecular mass are 10^5 , 10^5 - 10^6 and $>10^6$ for low, medium and high molecular mass polymers respectively. All polymers used as flocculants in water treatment must be water

soluble. In aqueous solution, polymers adopt a random coil configuration (Fig.1).

For very high molecular weight polymers, the size of coil is typically in the order of hundreds nanometer. If polymer chain is fully stretched, then end to end distance "r"

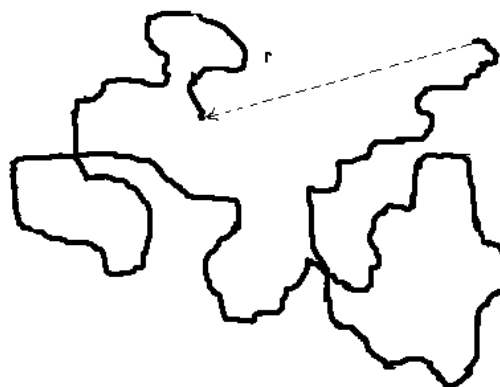


Fig.1 : A polymer chain in a random coil configuration the end to end distance is r.

can be up to $10\mu\text{m}$ or more. This is generally unlikely arrangement. The random coil is the most common configuration. The extent of random coil depends upon the interaction between polymer segments. If there is appreciable repulsion between segments then the coil expands. The most obvious examples are those polyelectrolytes where the segments are charged. In this case, the polymer coil can be significantly expanded and there can be important ionic strength effects. At high ionic strength, the repulsion between the charged segments is screened by ions in solution and so the coil expansion is not so great. As the salt concentration is reduced, repulsion becomes more significant and polymer coil adopt more expanded configuration which can be seen in (Fig-2).

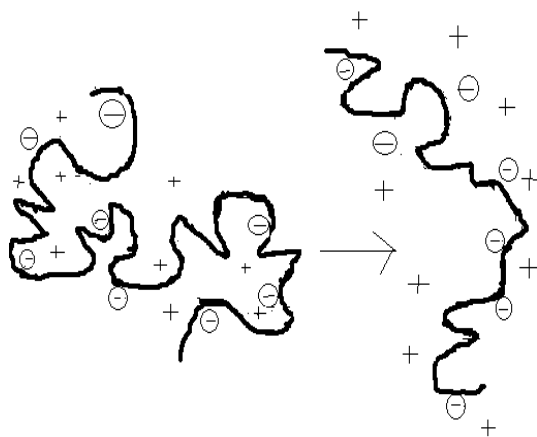


Fig.2 : Showing the expansion of a polyelectrolytes chain with decrease of ionic strength.

In case of polyelectrolytes, charge density is also a very significant parameter. Charge density can be expressed in terms of mole percent of charge groups or as meq/g. For example, we can calculate the charge density from the molecular mass of monomer units. In case of 100% cationic polyelectrolytes such as poly allyl dimethyl ammonium chloride, charge density follows directly from the molecular wt of monomer units (162), since one gram of polymer has 1/162 equivalent of charge. Hence, the charge density is 6.2meq/g. Broadly charge density values are regarded as low, medium

or high if the mol % of ionic groups are 10%-25%, 25%-50% and >50% respectively. According to cationic and anionic charge density, they are divided into cationic and anionic polyelectrolytes.

Cationic Polyelectrolytes:

They are having cationic charge density, and satisfy the cationic demand of the negatively charged suspended particles and initiate coagulation and flocculation process. There are many variety of cationic polymers available^{14,15}. Usually they possess quaternary ammonium groups that have a positive charge and termed as a strong positive electrolyte polymers¹⁶. Some of the synthetic polyelectrolytes are polydiallyl dimethyl ammonium chloride (PDADMAC), Epichlorohydrine polymers and cationic poly-acrilamides. PDADMAC is water soluble and low to medium molecular mass polymers whereas Epichlorohydrine polymers form polymers with ammonia and primary and secondary amines, in which the active sites are quaternary ammonium group. Cationic polyacrilamide is generally used in water industry^{17,18}. The cation content in the cationic PAMS can be in the range of 10-80%.

Table 1: Formulation and charge density of some cationic polyelectrolytes

Mol. formula	Charge density(mol%)	Charge density (meq/g)
$C_8H_{16}NCl$	100	6.2
$C_5H_{12}ONCl$	100	7.3
$C_8H_{16}O_2NCl$	100	5.2
$(C_8H_{16}O_2NCl)_{0.5}(C_3H_5ON)_{0.5}$	50	3.8
$(C_8H_{16}O_2NCl)_{0.5}(C_3H_5ON)_{0.5}$	25	2.5
Chitosan	100	5.2

There are several naturally occurring polymers that have inherent cationic properties or modified to yield cationic properties^{19, 20}. The most prominent ones are chitosan and starch. Starch is a polymer composed of α -D glucose units and can be converted to cationic derivatives. Table-1 shows the formulation and charge density of some of the cationic polyelectrolytes.

Anionic Polyelectrolytes

They are generally differentiated by a functional group²¹. They are generally manufactured by co polymerization of acrilamide and acrylic acid. The most commonly used anionic polyelectrolytes contain weak acidic carboxyl groups. High

molecular weight carboxylic polymers derived from PAM are extensively employed as flocculating agents in the water and other process industries.

Some natural anionic polyelectrolytes are also available such as many sulphated polysaccharides. The examples of sulphated polysaccharides are heparin and dextran sulphate. But as per literature survey, their application is only medical based. The natural polyelectrolyte which is under discussion among the scientists for water quality improvement is tannin²². Some of the important anionic polyelectrolytes are listed in Table-2 in terms of charge density as mol% and calculated on a theoretical basis in meq/g of polymer.

Table 2: Formulation and charge density of some of the anionic polyelectrolytes

Mol. formula	Charge Density (mol%)	Charge density(meq/g)
$C_3H_3O_2Na$	100	10.6
$(C_3H_3O_2Na)_{0.75}(C_3H_5ON)_{0.25}$	75	8.5
$(C_3H_3O_2Na)_{0.50}(C_3H_5ON)_{0.50}$	50	6.1
$(C_3H_3O_2Na)_{0.25}(C_3H_5ON)_{0.75}$	25	3.3
$(C_3H_3O_2Na)_{0.1}(C_3H_5ON)_{0.9}$	10	1.4

Polymer bridging and Charge neutralization

Mechanism of flocculation of particles by polyelectrolytes can be described under two headings: Polymer bridging and Charge neutralization which includes electrostatic patch effects²³. These two effects are crucially important for mechanism of flocculation.

Polymer adsorption: If there is some affinity between polymer segment and a

particle surface, then adsorption of polymer chain may occur. Polyelectrolytes with a charge opposite to that of surface adsorb oppositely charged ionic groups. For example, cationic polyelectrolytes adsorb strongly on negative surface, whereas anionic polyelectrolytes can adsorb on negatively charged surfaces despite electrostatic repulsion. This can only occur when there is sufficient concentration of divalent metal ions. For example, Ca^{2+} can act as bridge between anionic groups on the polymer and negative sites on the surface.

But in the absence of divalent cations, no flocculation occurs, even at high ionic strength.

Polymer bridging

An essential requirement for bridging flocculation is that there should be sufficient unoccupied surface on the particle for attachment of segments of polymer chains adsorbed on other particles²⁴. The adsorbed amount should not be too high, otherwise the particle surfaces will become so highly covered that there will be insufficient adsorption sites available²⁵. Polymer bridging can be seen in figure-1 (a & b). If adsorbed amount is too low then, polymer bridging will not be formed. This leads to an idea of optimum dosage for bridging flocculation. Typical optimum dosages in practical systems are in the order of 1mg polymer / g of suspended solids. It is generally found that most effective polymers for bridging are linear chain of high molecular weight. Charge density has large influence on bridging effectiveness. Very strong flocs are formed by bridging but broken flocs may not easily regrow.²⁶

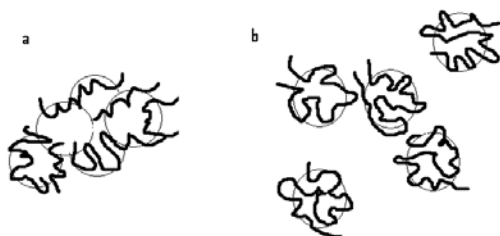


Figure 3 : (a) Bridging flocculation
(b) Destabilization of adsorbed chain

Charge neutralization

In most of the cases, suspended particles are negatively charged that's why it has been found that cationic polyelectrolytes

are the most effective flocculants. Electrostatic interaction gives strong adsorption in this system²⁷. It has been found that polyelectrolytes of high charge density are more effective because for a given dosages; they deliver more charges to the particle surface. Since high charge density polymers tend to adsorb in a rather flat configuration and there is little opportunity for bridging interactions. When high charge density polyelectrolytes adsorb on negative surfaces with low density of charged sites, then electrostatic patch mechanism will develop which can be seen in figure- 4. This model was independently suggested by Gregory²⁸ in 1973.

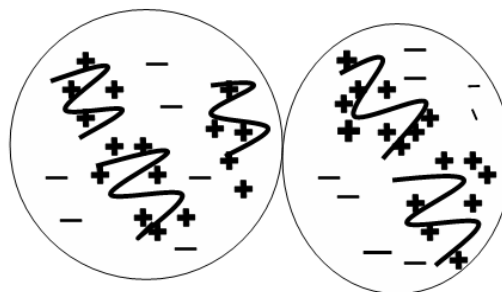


Figure 4 : Electrostatic patch model for flocculation.

There is electrostatic attraction between positive patches and negative areas, which can give particle attachment and it leads to flocculation²⁹. Flocculation formed by this way is not as strong as by bridging. Re-flocculation after flocculation breakage occurs more readily in electrostatic patch than in polymer bridging. The summary of mechanism of polyelectrolytes in terms of different parameters has been tabulated in Tab-3.

Table-3: The summary of mechanism of polyelectrolytes

Serial no	Parameters	Bridging	Electrostatic patch mechanism
1.	Molecular. mass of Polyelectrolytes	Higher the mol. mass, more effective is the bridging.	Mol. mass does not have much effect
2.	Charge density	Bridging more effective at higher charge density due to larger loop.	Higher the charge density, more effective will be destabilization
3.	Polyelectrolytes of similar charge to particle surface	Destabilization by bridging mechanism	Inoperative
4.	Polyelectrolytes of opposite charge to particle surface	Destabilization by bridging mechanism	Destabilization by electrostatic patch mechanism possible
5.	Nonionic polyelectrolytes	Destabilization by bridging mechanism	Destabilization by electrostatic patch mechanism inoperative
6.	Ampholytic Polyelectrolytes	Destabilization by bridging mechanism possible	Destabilization by electrostatic mechanism possible

CONCLUSION AND DISCUSSION

There are various methods for removing turbidity. Some stabilized chemical coagulants were tried earlier under different conditions for turbidity removal. But results have shown that they are partially successful in removing turbidity. So the present study explores the advantages of use of polyelectrolytes in water treatment. It is being found that polyelectrolyte can do this job in excellent way if proportioning is done in optimum manner.

Work so far has revealed that high charge density polymers with least polar structure are most effective in removing dissolved organic matter. Cationic charged

polyelectrolytes seems to be more effective for the removal of suspended particles. In fact cationic charged polyelectrolytes facilitate the destabilization and agglomeration of suspended colloids by neutralizing their surface charges, whereas if polyelectrolytes are having similar charges to the particle surface then destabilization generally occurs by bridging mechanism. In summary, it can be said about the bridging that high molecular weight and linear polymers are most effective and only a limited adsorbed amount of polymer is needed in bridging lest excess level can give restabilization. The ionic strength also plays an important part and presence of some divalent metal ions can be very important for

bridging, although it does not have much effect in electrostatic patch mechanism. Work so far revealed that with many advantages that polyelectrolytes have in water treatment, their usage is recommended, although more quantitative research is necessary on this aspect.

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APPENDIX

Turbidity removal mechanism:/ Kinetic aspects:

When polyelectrolytes are added in the suspended particles, several processes are initiated which have been discussed below.

Mixing: It is an essential process in which polymer is distributed evenly through out the suspension. The process of mixing is generally achieved rapidly otherwise excess concentration will give non uniform adsorption and some particles may re - stabilize as a result of adsorbing excess amount of polyelectrolytes. Poor mixing is generally responsible for residual haze in water after polymer flocculation and sedimentation. For proper mixing, a high degree of turbulence is desired, although some scission of polymer chains may occur under this condition. The rapid mixing generally has major effects on the flocculation process. Mixing effect is generally more important for more concentrated suspension.

Adsorption: The attachment of polymer chain to particles happens at a rate which generally depends upon the concentration. If particle concentration is increased, the

optimum polymer dosage will also increase proportionally. For low molecular weight polymers adsorption depend mainly on diffusion, but with high molecular weight flocculants shear induced collisions between polymer molecules and particles become more important. The rate of polymer adsorption depends upon mixing condition. For low turbidity waters, the time required for adsorption of polymers can be of the order of minutes, whereas for high turbidity water, adsorption time can be less than 1 second.

Rearrangement of adsorbed chain

A polymer chain adsorbed on a particle is needed to be arranged. A polymer chain reaches its equilibrium adsorbed configuration with characteristic distribution of loops, trains and tails. The time required for rearrangement of adsorbed chains depends upon a number of factors, although a little information is available in the literature about rearrangement of adsorbed chain. For high molecular weight polymers, time of several seconds may be needed, during which time adsorbed polymer has a more extended configuration than in the final equilibrium arrangement; that's why it readily forms bridging contacts. Pelssers²⁹ et al developed a kinetic model in term of active and inactive adsorbed polymer chains, in which active polymer chain is having extended configuration whereas inactive one is flattened on the surface. If low molecular weight polymer is pre-adsorbed on particles to give around 50% coverage, then flocculation by a high molecular weight polymer is much improved. This may be possible because a second polymer adopts a

more extended adsorbed configuration, since the pre-adsorbed configuration polymer makes many surface sites unavailable to the second polymer³⁰.

Flocculation

When particles have acquired enough adsorbed polymer to become destabilized then collision results in attachment, either by bridging or by electrostatic mechanism. For high solid concentration, flocculation rates may become very high. All flocculation process is carried out under some form of applied shear in the stirred tank or in the flow through reactor. In case of high mol weight polymers, adsorption time may be considerably longer than particle collision

times, so that adsorption may be the rate determining steps.

The particle collision time relative to the re-conformation time also needs to be considered. If the former is quite short then particles are likely to collide before the adsorbed polymer has achieved its equilibrium configuration and so is more extended from the particle surface. It generally occurs in more concentrated suspension. Bridging interaction most likely gives the possibility of non-equilibrium flocculation. In case of cationic polyelectrolytes and negative particles, bridging may occur in non-equilibrium phase but electrostatic patch flocculation would be more likely when the adsorbed chains are in a flatter configuration.